PB-240 939

WORKSHOP ON OZONE MEASUREMENT BY THE POTASSIUM IODIDE METHOD

John B. Clements

National Environmental Research Center
Research Triangle Park, North Carolina

February 1975

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1. REPORT NO. EPA-650/4-75-007	2. PB 240 939
4. TITLE AND SUBTITLE Summary Report: Workshop on Ozone Measurement by the Potassium Iodide Method.	5. REPORT DATE February 1975 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) John B. Clements, Ph.D., Chief, MSPEB/QAEML/NERC/RTP	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Methods Standardization & Performance Evaluation Branch Quality Assurance & Environmental Monitoring Laboratory Environmental Protection Agency, NERC Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. 1HA327 ROAP No. 26AAG 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same	13. TYPE OF REPORT AND PERIOD COVERED Summary Report 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

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16. ABSTRACT

The Federal Reference Method for photochemical oxidants specified in regulations on National Primary and Secondary Ambient Air Quality Standards is based on the chemiluminescence resulting from the reaction of ozone with ethylene. The method is calibrated by measuring synthetically prepared standard atmospheres of ozone and developing a method response vs. ozone concentration curve. The concentration of ozone in the standard atmospheres used for calibration is determined by using the 1% neutral buffered potassium iodide procedure specified in the regulations appearing in the Federal Register, 36, 84, Part II, 8186-8201, April 30, 1971 .

Although the 1% neutral buffered potassium iodide procedure has been used for sometime, it has been criticized for its inconsistent and non-reproducible results. These criticisms are of concern to EPA because they call into question the methodological basis for one of its regulatory standards and, likewise, NBS is concerned because there seems to be a national need associated with an important environmental measurement.

Therefore, a workshop on the problem was held Aug. 26-27, 1974, at NBS facility, Gaithersburg, Md., to bring together individuals with expertise in the use of the potassium iodide method for a full technical discussion of this ozone method calibration problem. This report presents recommendations and a summary of the discussions held at this workshop.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ozone measurement Potassium iodide procedure Chemiluminescent procedure Calibration		

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Springfield, VA. 22151

18. DISTRIBUTION STATEMENT Release unlimited	19. SECURITY CLASS (This Report) None	21. NO. OF PAGES 36
	20. SECURITY CLASS (This page) None	22. PRICE $3.75

PRICES SUBJECT TO CHANGE

EPA-650/4-75-007

SUMMARY REPORT: WORKSHOP ON OZONE MEASUREMENT BY THE POTASSIUM IODIDE METHOD

by

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ROAP No. 26AAG
Program Element No. 1HA327

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Publication No. EPA-650/4-75-007

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ACKNOWLEDGMENTS

Particular appreciation is expressed to Mr. E.E. Hunt of The National Bureau of Standards for making the arrangements to host the workshop. Especial acknowledgment is also expressed to Dr. J.A. Hodgeson for the original suggestion to hold such a workshop.

SUMMARY REPORT

WORKSHOP ON OZONE MEASUREMENT BY THE POTASSIUM IODIDE METHOD

INTRODUCTION

The Federal Reference Method for photochemical oxidants specified in regulations on National Primary and Secondary Ambient Air Quality Standards is based on the chemiluminescence resulting from the reaction of ozone with ethylene. The method is calibrated by measuring synthetically prepared standard atmospheres of ozone and developing a method response versus ozone concentration curve. The concentration of ozone in the standard atmospheres used for calibration is determined by using the one percent neutral buffered potassium iodide procedure as specified in the regulations appearing in the Federal Register 36(228):22384-22397, November 25, 1971.

Although the one percent neutral buffered potassium iodide procedure has been in use for quite some time, it has been widely criticized for its inconsistent and non-reproducible results. These criticisms are of considerable concern to EPA because they call into

question the methodological basis for one of its regulatory standards; likewise, NBS is concerned because there seems to be a national need associated with an important environmental measurement.

With these concerns in mind, a workshop on the problem was held on August 26 and 27, 1974, at the National Bureau of Standards (NBS) facility in Gaithersburg, Maryland, to bring together individuals with expertise in the use of the potassium iodide method for a full technical discussion of this ozone method calibration problem.

The purpose of the workshop was for the participants to exchange information and relate experiences on the problem and to propose recommendations on future actions. This report presents these recommendations and a summary of the discussions held.

WORKSHOP RECOMMENDATIONS

- EPA and others should continue research and development on the ultraviolet photometry method for measuring ozone.
- EPA and others should continue work on potassium iodide methodology for measuring ozone.
- NBS should develop a certified ozone standard.
- EPA and others should investigate other promising methods for measuring ozone.

WORKSHOP PARTICIPANTS

National Bureau of Standards

Radford Byerly, Jr.
Ernest E. Hughes
James R. McNesby
William P. Schmidt
John K. Taylor

Environmental Protection Agency

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Thomas A. Clark
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Kiyoshi Nishikawa

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Margaret Brunell

California Institute of Technology

William B. DeMore
Sigmund Jaffe

National Aeronautics and Space Administration

Harry M. Finley
(Old Dominion University)
J. David Kuder

DISCUSSIONS

The discussions were organized into four topic areas as follows: (1) Experiences with the Neutral Potassium Iodide Method; (2) Evaluation of the Neutral Potassium Iodide Method; (3) Absolute Measurement of Ozone; and (4) Proposals and Recommendations. Selected participants made a presentation on some aspect of the problem, then encouraged a full exchange of information. A brief summary of each presentation is given below and wherever appropriate salient points of discussion are recounted.

A. Experiences with the Neutral Potassium Iodide Method

1. Hodgeson: Dr. Hodgeson reviewed the important literature on the use of iodometry for the measurement of ozone concentrations (The literature references presented by Dr. Hodgeson are given as Appendix A of this report). He pointed out that the use of one percent neutral buffered potassium iodide is specified as the means to calibrate the Federal Reference Method for oxidants and is an integral part of the method. The potassium iodide calibration is a weak link as is shown by the poor comparison between measurements of ozone made by the one percent neutral potassium iodide procedure and by ultraviolet photometry and as shown by the inability of various workers to get consistent results.

2. Margeson: Mr. Margeson reported on the results of an interlaboratory collaborative test of the Federal Reference Method for oxidants. The test was carried out in two parts with the first part

designed to test the method's precision and the second part designed to test the method's bias.

In the test of the method's precision, a group of nine qualified participants were gathered together to measure the same ambient air at a single location (Pasadena, California) for a four-day period. The test results showed that the method has fairly good precision, in the range of 15-20%.

To test the method's bias, a number of ozone generators, which had been carefully calibrated by the National Bureau of Standards, were sent to test participants for them to make measurements of atmospheres prepared by these generators in their own laboratories. The test was designed so that the participants did not know the ozone concentrations they were generating. At the end of the test, the generators were returned to NBS for recalibration.

Nine participants made measurements at five levels of ozone; all measurements made by the participants were less than the corresponding calibration value, thus indicating a negative bias some place in the method. The following table summarizes the test results:

NBS Calibration Value (ppm)	0.05	0.08	0.13	0.28	0.50
Average Collaborator Bias	-37%	-31%	-26%	-17%	-16%

Mr. Komhyr pointed out that the output from an ozone generator is pressure dependent. The pressure dependency is not necessarily linear over wide pressure ranges and this would affect calibration values at higher elevations, for example, Denver, Colorado.

3. Beard: The apparent bias in the Federal Reference Method led to an investigation by NBS and EPA into its causes. The potassium iodide calibration was immediately suspected and Mr. Beard reported on experiments which seemed to implicate the impinger used to contain the potassium iodide as one important source of this bias. NBS and EPA teams, using their own reagents and apparatus to sample a common ozone atmosphere, have shown that the set of impingers used at NBS for calibrating generators used in the collaborative test give consistently higher ozone values than do other impingers. Mr. Beard described an experiment in which a constant ozone atmosphere of about 0.2 ppm was established, and the bubbler-type impingers specified in the Federal Reference Method were used by EPA for sampling and midget impingers were used by NBS for sampling. There was also a feature in the experiment in which the EPA worker used the midget impinger for sampling, but used his own reagents and spectrophotometer. The following results were obtained:

Impinger Design	Ozone Found (ppm)	Analyst
Federal Reference Method	0.201	EPA
	0.203	EPA
	0.204	EPA
NBS Midget Impinger	0.230	NBS
	0.236	NBS
	0.234	EPA
	0.241	EPA

Mr. Beard also reported an investigation in which various levels of ozone, up to about 1 ppm, were measured using bubbler impingers and midget impingers at each level. These experiments indicated that the midget impingers find approximately 1.2 times more ozone than do the bubbler-type impingers.

4. Hughes: Mr. Hughes has studied a number of midget impinger pairs and has found one particular set, designated 1 and 1A, which consistently gives higher ozone values than does any other set. Some idea of the differences is shown by comparing this set with several other sets and assuming a collection efficiency of 100% for 1 and 1A:

Impinger Designation	Collection Efficiency
1 and 1A	100%
3 and 3A	Ca. 90%
4 and 4A	Ca. 95%
5 and 5A	Ca. 95%

Mr. Hughes has studied a large number of factors, including impinger design features and other aspects of the method, which might cause the high results found for 1 and 1A. The following factors were studied:

Interchanging impinger parts; varying the orifice diameter; varying the distance from the tip of the orifice to the bottom of the container, doubling the solution volume from 10 ml to 20 ml; varying flow rate from 0.6 l/min to 2 l/min; investigating iodine volatilization (by using a modified Bergshoeff procedure); measuring absorbance immediately at the end of the sampling and 30 minutes after end of sampling; increasing pH from

6.83 to 8.86; varying the age of potassium iodide solution; and using triple distilled water. Unfortunately, none of the variables studied had a significant effect, and the reason for the bias is still not evident.

Dr. Hodgeson suggested that iodate formation caused by the catalytic effect of surfaces at neutral pH may explain some of the differences between impingers (see Parry and Hern, Reference 10, Appendix A).

5. Tokiwa: The Air and Industrial Hygiene Laboratory has compared its potassium iodide ozone calibration procedure (which is also the one used by the California Air Resources Board) with the EPA procedure. A comparison of the twc procedures follows:

	EPA	AIHL
Absorber	2 bubblers	2 midget impingers
Absorbing solution	1% KI: pH = 7	2% KI: pH = 7
Sampling rate	0.2-1.0 l/min.	1 l/min.
Sampling time	10 min.	5 or 10 min.
Analysis	same	same

It is generally agreed that the biggest difference is the concentration of the potassium iodide.

Mr. Tokiwa reported that they had compared the two procedures experimentally and find very little difference between them. He also reported experiments in which the sampling time, collection efficiency, and period to maximum color formation were studied. There were also some experiments which compared impingers and frits when each system

was used with two devices in series. The following tables present the results:

Sampling time, minutes	Nominal O_3 Conc., ppm	Collection Efficiency, % Impinger 1	Frit 1
10	0.14	97-100	97-100
10	0.52	95	95
30	0.14	90-93	89

		% Color Developed at Indicated Times			
		1 min.	5 min.	15 min.	20 min.
10	0.14	-	94-97	100	-
10	0.52	91-93	93-95	-	100

Mr. Tokiwa recommends that two impingers be used and that the analyst wait 15 minutes for color development.

Mr. Hughes commented that in his studies, in which he uses one percent neutral potassium iodide, approximately 10% of the ozone is collected in the second impinger. Mr. Tokiwa said that their 2% potassium iodide system characteristically collects at least 95% of the ozone in the first impinger. There was general agreement that the higher potassium iodide concentration in the AIHL system is probably the basis for its better collection efficiency.

Mr. Tokiwa also reported that they always check their potassium iodide for the presence of a reducing agent that is added to some grades in order to keep them white. This additive, if not accounted for, causes an unknown iodine demand and leads to erroneous results. They have found

that USP grade potassium iodide does not contain this additive and gives satisfactory results in their hands.

6. Brunelle: Mrs. Brunelle recounted the history of monitoring for oxidants carried on by the Los Angeles County Air Pollution Control District, pointing out that the District had used a monitoring system based on the reaction of oxidants with unbuffered potassium iodide reagent. For calibration, they investigated buffered and unbuffered 20% potassium iodide reagent, but found high blank values. They also studied 2% unbuffered potassium iodide and found no blank problems and also found that the end point in the thiosulfate titration they use is easier to determine in the 2% system. All of these reasons led them to select the 2% unbuffered potassium iodide system for calibration as their standard procedure

Mrs. Brunelle stated that an absolute reference method or standard material for ozone is urgently needed--one that would permit the intercomparison of the various ozone measuring techniques. This view was supported strongly by other members of the conference.

B. Evaluation of the Neutral Potassium Iodide Method

1. Hodgeson: Dr. Hodgeson reported on work carried out in his laboratory in which various factors influencing the absorbance values of the iodide-iodine collection reagent were investigated. He also reported on investigations in which ozone concentrations measured by the 1% neutral buffered potassium iodide procedure were compared with ozone measured by ultraviolet photometry. A number of graphs presented

by Dr. Hodgeson are reproduced in Figures 1 through 4 in a schematic and non-quantitative fashion in an effort to summarize the major findings.

Figure 1 presents the decay of absorbance of standard iodide-iodine solutions with time, implying that color stability is a problem. Figure 2 presents the change in absorbance of ozonized potassium iodide solutions as a function of time. Mr. Tokiwa and Mr. Hughes both remarked that they have observed the same phenomenon, and Dr. Jaffe said that he has also observed that the decay in absorbance continues at times beyond 60 minutes.

Figure 3 presents the change in absorbance for potassium iodide solutions as a function of the potassium iodide concentration. Two levels of ozone were examined.

Figure 4, which shows the ratio of ozone concentration as measured by potassium iodide and by the Dasibi instrument as a function of sampling time, also shows the ratio of the color in the second sampling impinger (A_2) and the total color in both impingers (A_t) as a function of sampling time. In these experiments, the ozone concentration was 0.6 ppm and sample flow rate was 0.5 ℓ/min. Apparently, volatilization of iodine is important as is shown by the decrease in the $[O_3]_{KI}/[O_3]_{UV}$ ratio and the increase in the A_2/A_t ratio, particularly after 30 minutes of sampling.

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A study of impinger components showed that there seems to be very little effect on the change in ratio of ozone measured by potassium iodide and by ultraviolet photometry with change in impinger design. The following relationships were developed:

(1) Wide impinger orifice, poor impinger action

$$[O_3]_{KI} = (1.070 \pm 0.021)\,[O_3]_{UV} - 0.017$$

(2) Narrow impinger orifice, good impinger action

$$[O_3]_{KI} = (1.087 \pm 0.018)\,[O_3]_{UV} - 0.017$$

The similarity of the slopes and intercepts of the two equations shows that the features studied have little effect.

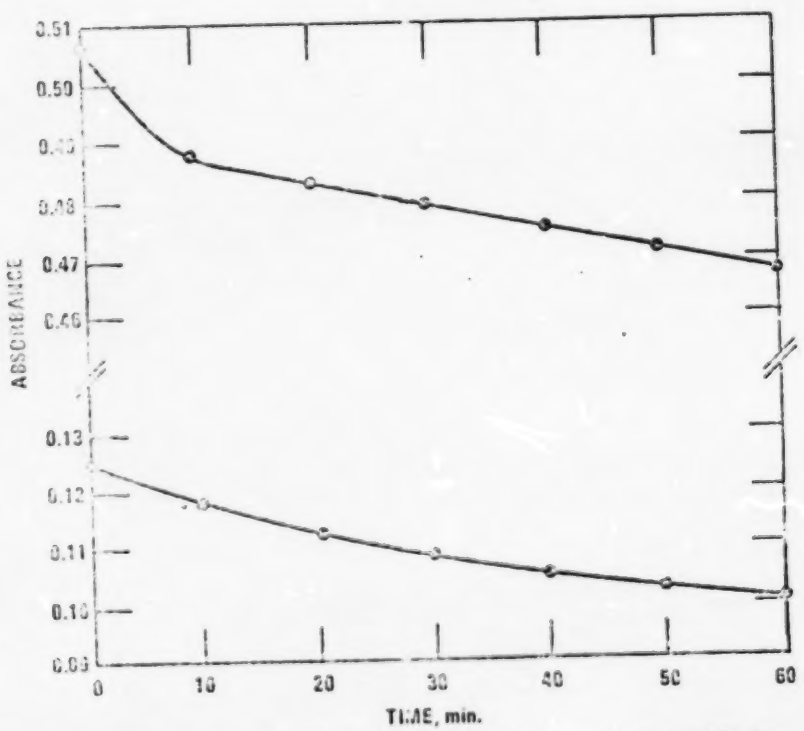

Figure 1. Change in absorbance of iodide - iodine solution with time.

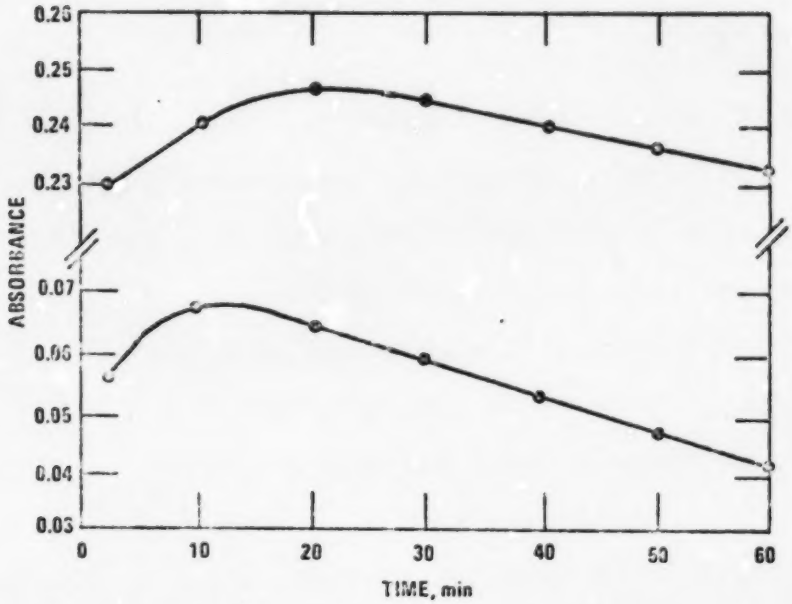

Figure 2. Change in absorbance of ozonized solution with time.

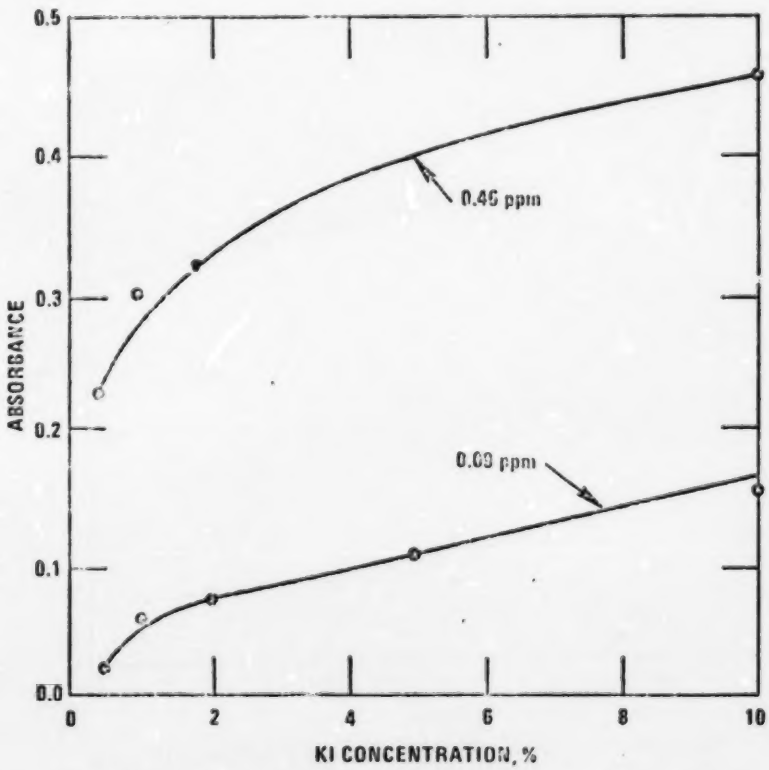

Figure 3. Change in absorbance with KI Concentration at constant ozone concentration.

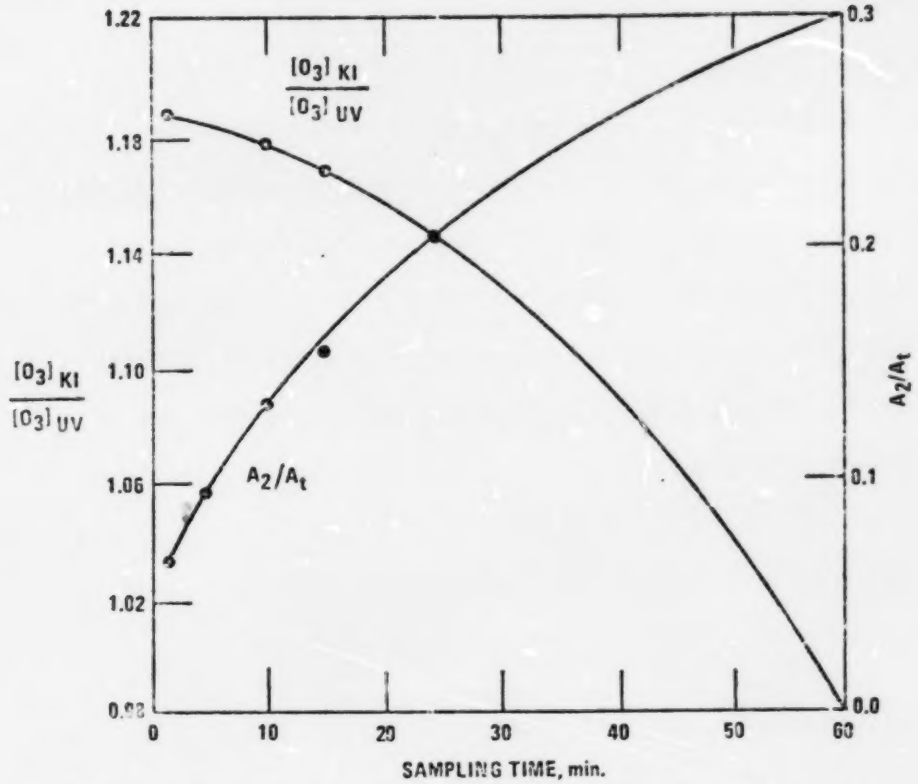

Figure 4. Comparison of ozone by KI and by UV and comparison of absorbance as a function of sampling time.

2. Jaffe: Dr. Jaffe reported experiments designed to compare ozone measured by iodometry and by ultraviolet photometry. He described his apparatus, which contained a photometer and a Dasibi ozone monitor and which allowed the concurrent measurement of ozone by ultraviolet photometry and by the potassium iodide procedure.

The ozone concentrations studied range from 1 or 2 parts per million to 15 or 20 parts per million. Figures 5 and 6 portray in a schematic and non-quantitative fashion the important findings reported by Dr. Jaffe.

Figure 5 shows a comparison of the ozone concentration as measured by ultraviolet photometry and by potassium iodide. Figure 6 shows the relationship of the ratio of ozone measured by KI (as shown by concentration of I_3^- measured) and by UV as a function of concentration. This experiment is evidence that the stoichiometry of the reaction of ozone with potassium iodide changes from one to one to a higher value, and the change seems to occur at about 2 ppm ozone.

Dr. Jaffe offered the opinion that we could reasonably look to a standard for ozone based on ultraviolet photometry.

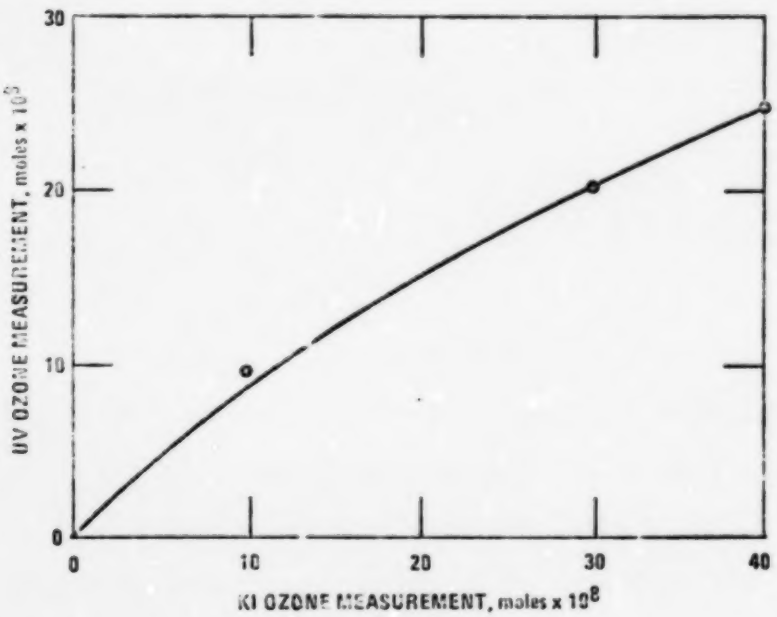

Figure 5. Ozone by UV and KI.

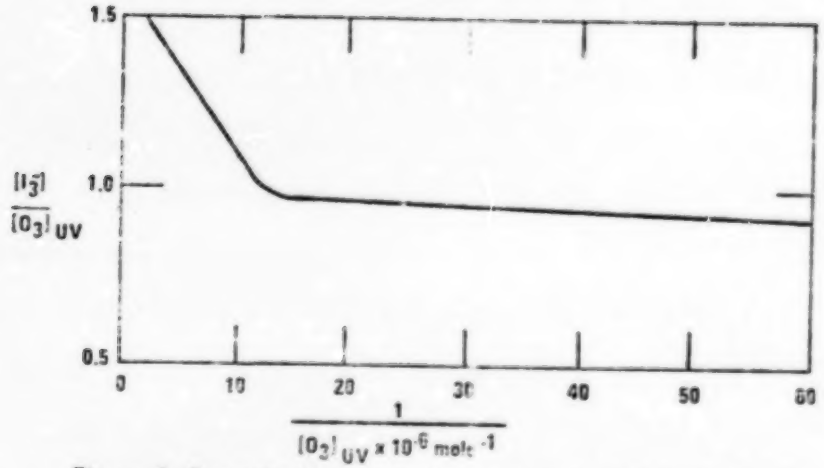

Figure 6. Ozone by KI and by UV as a function of ozone concentrations.

3. Rehme: Mr. Rehme reported on research in which the rapid and quantitative reaction of nitric oxide with ozone is the basis for making ozone measurements. The reaction of interest is:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

This reaction is used to calibrate an ozone generator in the following way:

A level of NO, generally about 1 ppm, is established using a cylinder of nitric oxide, generally about 100 ppm, which has previously been analyzed. The NO level is monitored continuously. Ozone from a stable source is added in increments and the decrease in NO response corresponds, according to the above equation, to the amount of ozone added. A calibration curve can then be constructed for the ozone source, and it then serves as a device which can produce, on demand, atmospheres

containing known concentrations of ozone. The term gas phase titration is used to describe the process.

Until recently a weakness in the procedure has been the measurement of the nitric oxide concentration in the cylinder using gas phase titration in a configuration somewhat as described above. In this configuration known levels of ozone are reacted with NO and the results used to determine the NO concentration in the cylinder. The known levels of ozone are based on iodometry which is where the weakness resides.

Mr. Rehme described one approach that has been used to obviate this problem. The NO level of the cylinder has been related to the output from a NO_2 permeation device which has been gravimetrically calibrated. A NO_x monitor, in which NO_2 can be quantitatively converted to NO, is required. Mr. Rehme reported that agreement of 3% or better can be obtained between NO assays based on the ozone-nitric oxide gas phase titration and NO assays based on the gravimetrically calibrated NO_2 permeation device.

4. Stevens: Mr. Stevens described experiments currently under way in his laboratory which will compare the 1% neutral buffered potassium iodide procedure (the EPA Reference Method procedure), the 2% neutral buffered potassium iodide procedure (the California Air Resources Board procedure), and the 2% unbuffered potassium iodide procedure (the Los Angeles County Air Pollution Control District procedure) by having them all sample the same ozone atmospheres simultaneously. Several

levels will be studied and at each level an independent assay of the ozone concentration will be made by gas phase titration and, he hopes, by ultraviolet photometry.

Mr. Stevens emphasized again the acute need for an ozone standard of some sort. In this context, Dr. Taylor of NBS expressed confidence in gas phase titration as an approach.

C. Absolute Measurement of Ozone

1. DeMore: In their studies on reaction mechanisms, Dr. DeMore pointed out that they have a need to know fundamental constants and in this connection have done considerable work on the extinction coefficient of ozone. The coefficient has been determined for ozone at various pressures down to a few torr and does not seem to have any dependency on pressure. This leads to the conclusion that the extinction coefficient at ppm levels should be the same, and Dr. DeMore described experiments in which optical density was measured under the conditions of a few torr and under the conditions of a few ppm ozone. The ratios of the corresponding extinction coefficients are constant as the following table shows:

Experiment No.	OD torr	OD ppm	E torr/Eppm
1	0.29	0.0325	0.97
2	0.53	0.062	1.01
3	0.81	0.095	1.01
4	1.31	0.165	1.04
5	1.49	0.180	1.06

Dr. DeMore does not believe the ratio is showing a trend. The ozone level for the first experiment is about 3 ppm; the others are higher levels of ozone.

Dr. DeMore described experiments in which ozone measurements made by a laboratory photometer were compared to ozone measurements made by a Dasibi instrument. His experiments indicate that Dasibi measurements are about 3.5% lower than the photometer measurements at the ozone concentrations studied.

Dr. DeMore also noted that the temperature in a Dasibi instrument runs about 10-15^{o}C higher than ambient and said that this temperature difference should be taken into account when comparing ozone measurements made by a Dasibi and a laboratory photometer.

2. Komhyr: Mr. Komhyr's agency had a need to make ozone measurements into the stratosphere and at clean air locations on the earth's surface. For this purpose he developed a device, called the electrochemical concentration cell (ECC) ozone sensor, which is based on the electrochemical oxidation of iodide ion to tri-iodide ion and the measurement of the current produced. The appropriate reactions are:

$$3I^- \longrightarrow I_3^- + 2e \qquad \text{Oxidation}$$

$$I_2 + 2e \longrightarrow 2I^- \qquad \text{Reduction}$$

The overall cell reaction is:

$$3I^- + I_2 \longrightarrow I_3^- + 2I^-$$

No external e.m.f. is applied to drive the cell since the highly different electrolyte concentrations in the cell's cathode and anode chambers (approximately 0.1 molal and 8.0 molal, respectively) give rise to a spontaneous driving e.m.f. defined at 25°C by:

$$E = -\frac{0.0591}{2} \log \frac{(a_1)_{I_3^-}}{(a_4)_{I_2}} \cdot \frac{(a_3)^2_{I^-}}{(a_2)^3_{I^-}}$$

where the a's are ionic activities.

The stoichiometric properties of the cell are dependent to a small extent on the KI concentration of the cathode electrolyte. A doubling of the electrolyte KI concentration, for example, increases measured ozone amounts by 5%. Mr. Komhyr described tests in which atmospheric total ozone amounts derived from ECC ozonesonde ascents into the stratosphere were compared with atmospheric total ozone amounts derived quasi-simultaneously by spectroscopic means using Dobson ozone spectrophotometers. The tests showed agreement in measured total ozone amounts by the two independent methods when 1.5% KI electrolyte solutions were employed in the cathode chambers of the ECC cells.

Some data were presented on the reproducibility of the cell's performance over a long period of time. In view of the simplicity in preparing for use and using the ECC ozone sensors, Mr. Komhyr suggested that the devices may be usefully employed in periodic checking of calibrated ozone generators.

3. Hodgeson: Dr. Hodgeson described experiments carried out in his laboratory, which related ozone concentrations as measured by iodometry and by ultraviolet photometry. Figure 7 shows the relationship of ozone as measured by neutral potassium iodide and by ultraviolet photometry using a one-meter path-length cell. Measurements were made between 1 and 12 ppm, and the ratio of ozone concentrations measured by potassium iodide to the ozone concentration measured by photometry approaches unity below 1 ppm. The regression equation for the data is:

$$[O_3]_{KI} = 1.093 \pm 0.006\ [O_3]_{UV} - 0.035 \pm 0.021$$

Figure 8 shows the relationship of ozone as measured by a Dasibi instrument and by a photometer. Concentrations determined by the Dasibi instrument are absolute values based on a logarithmic form of Beer's Law and an assumed cell path length of 71 cm. The regression equation for the data is:

$$[O_3]_{Dasibi} = 0.954 \pm 0.003\ [O_3]_{Photometer} - 0.027 \pm 0.008$$

Dr. Hodgeson described his use of NBS standard spectrophotometer filters as a means for checking spectrophotometer calibration. This has proven to be a very simple calibration check which may be used to supplement the tedious chemical calibration procedure. The stability which can be achieved with a DU-2 spectrophotometer is illustrated by the data of Table 1. Dr. Hodgeson suggested that the determination of the absolute absorption coefficient of iodine in 1% potassium iodide combined with the use of NBS standard filters has the potential to replace conventional wet chemical calibration procedures.

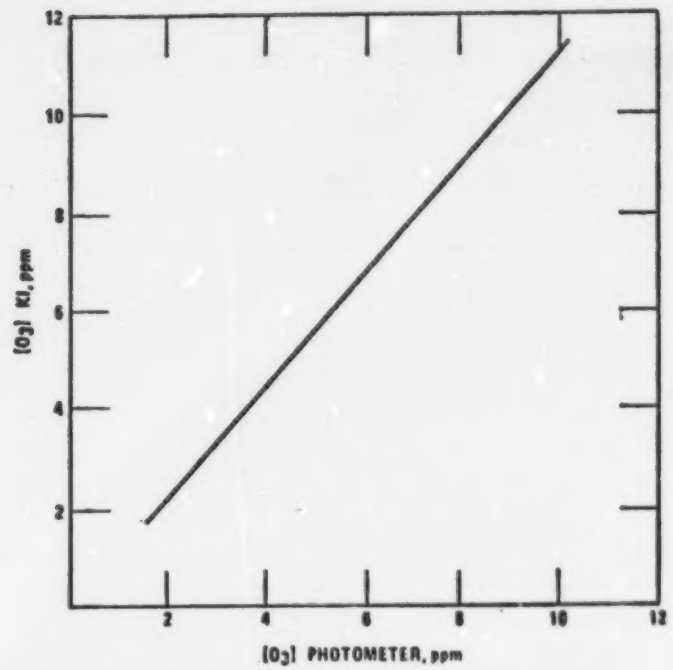

Figure 7. Comparative ozone measurements by neutral KI and UV photometry.

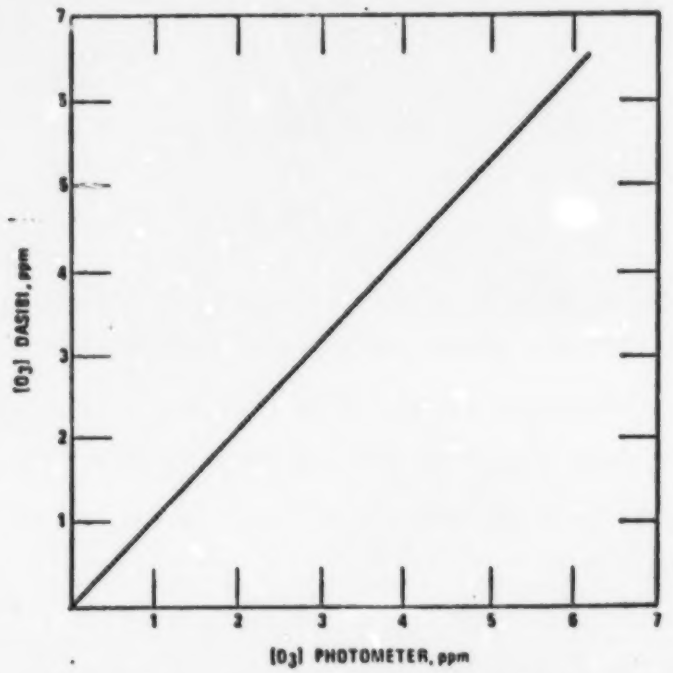

Figure 8. Comparative ozone measurements by 1-meter photometer and by Dasibi instrument.

Table 1. SPECTROPHOTOMETER CHECK WITH NBS STANDARD FILTERS

	Filter No. 3-163			
Date	λ, nm	Labeled Abs.	Meas. Abs.	Δ, %
1-29-74	440	0.512	0.513	-0.20
	465	0.467	0.468	-0.21
	590	0.516	0.514	+0.39
	635	0.502	0.499	+0.60
2-6-74	440	0.512	0.512	0
	465	0.467	0.467	0
	590	0.516	0.513	+0.58
	635	0.502	0.499	+0.60
2-12-74	440	0.512	0.505	+1.37
	465	0.467	0.458	+1.93
	590	0.516	0.506	+1.94
	635	0.502	0.492	+0.60
5-7-74	440	0.512	0.510	+0.39
	465	0.467	0.463	+0.86
	590	0.516	0.511	+0.97
	635	0.502	0.492	+0.80
8-8-74	440	0.512	0.516	-0.78
	465	0.467	0.470	-0.64
	590	0.516	0.518	-0.39
	635	0.502	0.498	+0.80

4. McClenny: Dr. McClenny described experiments by himself and co-workers to make absolute measurements of ozone using ultraviolet photometry. The goal of these experiments is to provide a simple, inexpensive UV photometer for use with an ozone generator. Such a combination would provide an alternative to the KI technique, if one is needed.

Dr. McClenny emphasized the need to eliminate scattered light in the photometer systems. Two UV photometers using folded optical paths were discussed, one employing a double-pass cell and the other a multipass "white" cell. Since the number of passes can be changed in the "white" cell, contributions to the output signal from scattered light can be checked. Thus, an absolute photometric measurement can be made by checking the agreement at more than one total optical pathlength, i.e., by ensuring internal consistency of the measurement.

Measurements were presented to illustrate the sensitivity of the double-pass photometer. Even though typical UV sources drift, linear drift can be eliminated by proper processing of the signal. To illustrate this, measurements over the ambient range 50-500 ppb were presented showing standard deviations of less than 5 ppb.

5. Nishikawa: Mr. Nishikawa recounted the history of oxidant monitoring in California. The first method was based on the phenolphthalin procedure, but this was abandoned in 1952 because it did not really characterize air quality. The phenolphthalin procedure was replaced by continuous 20% potassium iodide instruments, which were used until 1968 when they changed to 10% neutral buffered potassium iodide.

With the advent of the National Ambient Air Quality Standards in 1970, they were again faced with the problem of chosing new monitors for oxidant for the 35 stations which would be required.

At the time when a decision was required, there was only one manufacturer of chemiluminescence instruments on the West Coast, and California's choice had to be between it and the Dasibi instrument. An evaluation of both instruments led to the finding that the type of chemiluminescence instrumentation available to them would be difficult to service and would require a logistically troublesome tank of ethylene. The Dasibi instruments did not have these disadvantages and they chose to purchase them for their network.

They now have 19 Dasibi instruments in operation. The California Air Resources Board is very anxious to maintain its data base, so that trends can be kept intact. For this reason, they are doing parallel sampling at a number of their stations with the 10% neutral buffered potassium iodide continuous instruments and the newly installed Dasibi instruments. The calibration system for both instruments is based on 2% neutral buffered potassium iodide. Mr. Nishikawa presented preliminary data, which showed excellent correlation between the Dasibi and 10% neutral buffered potassium iodide measurements at two sites.

D. Proposals and Recommendations

1. Taylor: Dr. Taylor discussed the NBS policy requiring that before they certify a reference material it must have been assayed by two independent procedures. He then presented the concept of having the NBS provide certified ozone generators and have this certification be based on at least two independent standards. A recalibration

service would be provided for the certified generators. In his concept, the ultraviolet photometer would serve as one independent measurement for certification of the ozone generator; gas phase titration based on a nitric oxide standard, which is nearing certification by NBS, would serve as the other independent measurement. The concept as developed by Dr. Taylor can be shown schematically as follows:

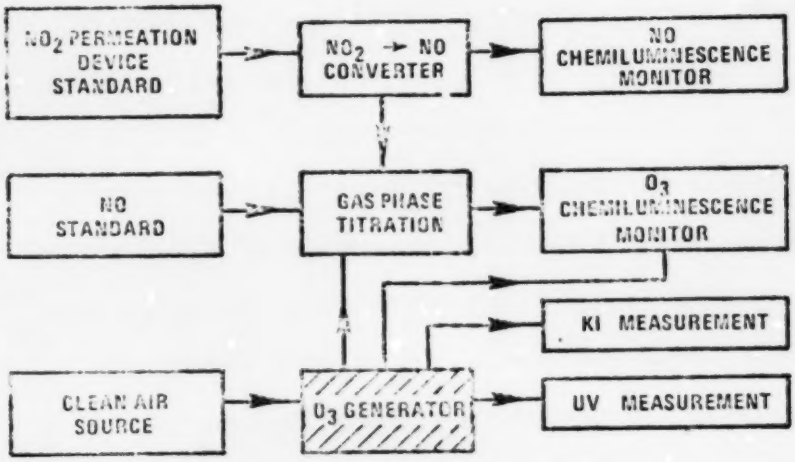

Figure 9. NBS proposed scheme for development of an ozone standard.

Dr. Hodgeson said he would be concerned that the generator could be transported and still retain its integrity. Dr. Taylor agreed that this is a prime consideration and said that the ruggedness of the device would be thoroughly tested and that methodology would be developed which would allow the recipient to relate his generator to one of the standards.

Other things suggested to be investigated were: effects of change in temperature and pressure from the point of calibration to the point of use, the quality of the air (particularly the oxygen content), and the need for voltage stabilization.

There was some sentiment that a ultraviolet photometer would be a viable approach to an ozone standard material. Dr. DeMore felt that it is reasonable to expect that a photometer, suitable as a standard, could be developed for the ambient range. Dr. McNesby seemed to be attracted to this idea. Dr. McClenny expressed interest in developing such a photometer and in having a number made for evaluation by EPA personnel.

Dr. Jaffe expressed the view that, while it is true that iodometry may have a place in ozone measurement, we should abondon the idea that potassium iodide is a satisfactory primary standard for ozone measurement, and we should look to other things. He suggests that ultraviolet photometry be seriously considered as a primary standard.

APPENDIX A

Dr. J. A. Hodgeson's References

(Statements given with the references are the salient features of the paper).

1. Custer and Natelson. Anal. Chem. 21: 1005, 1949 . Absorption spectra of trace I_2 in water, aqueous KI, organic solvents.

   λmax in KI at 352 and 289 nm

   Variation of α(352) with KI conc.

2. Birdsall, Jenkins and Spandinger. Anal. Chem. 24:662,1952. Compared iodometric ozone measurements with absolute ozone measured by gas density. Approximately 1.1 agreement between neutral KI and physical measurement (1-25% O_3). Acidic KI results 50% higher than neutral KI.

3. Byers and Saltzman. Adv. Chem. Series, No. 21, ACS (1959):93-101. The original article on 1% neutral KI technique and basis for EPA procedure assumes 1:1 stoichiometry based on earlier work. Alkaline KI results were 65% of neutral KI measurements.

4. Deutsch. J. Air Poll. Contr. Assoc. 18:77, 1968. Recommends an acid KI (pH = 3.8) technique for improved stability and freedom from interferences. Obtained 1:1 agreement between acid and neutral KI from 0.06 to 0.24 ppm O_3. Iodine losses from aerated acidic KI solutions noted.

5. Bergshoeff. Preprint, Pittsburgh Conference, 1970. Compared 5 spectrophotometric methods for O_3 measurement (neutral KI, Di(4-pyridyl ethylene), Diacetyl-dihydrolutidine, Dimethoxystilbene, indigotin-

disulfonate). Deduced 1:1 stoichiometry for neutral KI based on comparison. Modified the KI technique by adding excess thiosulfate to absorbing solution and performing back titration.

6. Boyd, Willis and Cyr. Anal. Chem. 42:670, 1970. Determined stoichiometry of neutral KI reaction by absolute UV photometric O_3 measurement. I_3^- formed/O_3 absorbed - 1.5 over range of about 50 to 1000 ppm. Used static KI measurement of O_3. Prepared chemical mechanism to account for different results in neutral and alkaline KI.

7. Hodgeson, Baumgardner, Martin and Rehme. Anal. Chem. 43:1123, 1971. Redetermined stoichiometry of ambient O_3 concentrations by gas phase titration of O_3 with known nitric oxide concentrations. Standard nitric oxide concentrations obtained from standard Scott cylinders, reanalyzed by Saltzman NO_2 technique.

$$I_3^- \text{ formed}/O_3 \text{ absorbed} = 0.98 \pm .07$$

8. Kopczynski and Bufalini. Anal. Chem. 43:1123, 1971. Measured absolute O_3 concentration by IR absorption and compared with neutral KI.

$$I_3^- \text{ formed}/O_3 \text{ absorbed} \simeq 1.0$$

9. Dietz, Pruzansky and Smith. Anal. Chem. 45:402, 1973. Determined absolute O_3 concentration by thermal decomposition - pressure differential measurement; measured a unity stoichiometry factor for high O_3 concentrations in neutral KI. By gas phase dilution obtained unity factor for sub-ppm concentrations.

Determined variations in stoichiometry with pH:

pH	I_3^-/O_3
4	1.06
7	1.02
9	0.99
12	0.95
14	0.80

10. Parry and Hern. Environ. Sci. Technol. 7:65, 1973.
Discussed significance of IO_3^- formation in O_3 - iodide reaction in neutral solution. Measured IO_3^- formation electrochemically. IO_3^- formation favored by high O_3 concentrations and catalytic effect of glass surfaces. IO_3^- formation usually insignificant at ambient O_3 concentrations.